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The Metallurgist.

Supplement to The Engineer, *June, 1934.*

Alloys of Iron Research.

THE Institution of Mechanical Engineers has recently circulated for written discussion copies of a paper in which Dr. Desch describes the work of the Alloys of Iron Research Committee. This paper comes very opportunely, and it is strongly to be hoped that the attention of metallurgical and engineering circles will be focussed for a time at any rate upon the invaluable research work which has been done at the National Physical Laboratory during the last few decades. The Alloys Research Committee of the Institution of Mechanical Engineers has been responsible for encouraging and financially supporting metallurgical research since 1890, *i.e.*, for a period of some forty-four years, and it would be an intriguing task to draw a comparative picture of the characteristics of the metals available for engineering construction in 1890 and in 1934. The work of the National Physical Laboratory, other institutions and universities at home and abroad, many private investigators of note, and the work of some of the industrial research laboratories have, during this period, greatly enriched metallurgical science; but it can, and indeed it must be said, that the heaviest contributions to technical progress in the form of new or improved alloys and steels have resulted from the empirical practical experimental work carried out in our industrial establishments. Many of these materials are complex in composition, their treatment and properties consistent, but their constitution insufficiently understood. It cannot be claimed that much of such progress was achieved by synthetically building upon the results of pure fundamental research. Neither can it be said that subsequently fundamental research has progressed sufficiently to explain or completely to evaluate the properties of many of the useful materials placed at the disposal of engineers as a result of the practical and empirical work to which reference has been made. That this is so, is not the fault of the Alloys Research Committee. That Committee has, within its resources, done much to assist in remedying the position, but vastly larger sums of money need to be placed at the command of such enlightened committees for the advancement of knowledge concerning our materials and the bases of their production.

The paper by Dr. Desch is an effective reminder of the valuable work which has been carried out by the Alloys Research Committee from the earliest days under the directions of Sir William Roberts-Austen, through the intermediate period under Dr. (now Sir) H. C. H. Carpenter, and the later period under Dr. Rosenhain and his successor Dr. Desch. Following upon the excellent work of Carpenter and Keeling upon the carbon-iron system, the N.P.L. workers have dealt with the alloys of iron with oxygen, phosphorus, silicon, chromium, and manganese, *i.e.*, with a number of binary systems. Only the simple binary systems have so far been seriously attacked, and the ternary, quaternary, and even more complex systems remain to be investigated.

Since the reports of the researches to which the paper refers have been previously published, it is perhaps unnecessary to comment critically, except to emphasise and to justify the need for the concurrent development of pure and applied science in relation to the industry; the former is essentially synthetic, the latter necessarily largely empirical. For instance, it is stated that whilst no two binary systems are alike, certain general relations emerge so that guidance is obtained as to the behaviour of systems containing more than two components. What are these general relations? We venture to state that at present the characteristics of ternary or higher systems cannot be reliably deduced from a study of the necessary binary systems, and hence the immediate need for greatly extending and intensifying research into many systems, either as yet untouched or only incompletely tackled. However elaborate and satisfactory the elucidation of the iron-carbon and iron-manganese system may have been, the remarkable and extremely useful properties of alloys in the iron-carbon-manganese system could not have been predicted. Again, it can be safely stated that a study of the iron-carbon-nickel and the iron-carbon-chromium systems would not have predicted the properties of invaluable alloys in the iron-carbon-chromium-nickel system.

The subsidiary and complementary investigations on refractories have given very useful results, and research workers and others will be grateful for the information now available concerning refractories which will stand up to certain arduous conditions of high-temperature work. Further work in this direction is, however, still required.

The general impression resulting from a study of Dr. Desch's paper is that an invaluable series of researches has been put through at the National Physical Laboratory. The deduction is obvious that were the resources available, there is here a great field of constructive fundamental research in metals, and it is much to be desired that steps shall be taken in the near future to ensure an adequate extension of the work.

The Metallurgy Research Board.

READERS of THE METALLURGIST are familiar with the name of the Metallurgy Research Board of the Department of Scientific and Industrial Research, and it should be of interest to them to hear something

of the workings of the Board, and, in particular, of the way in which it is now endeavouring to assist the metallurgical industries in a general attack upon problems which are hindering progress.

The Board is one of a number of similar bodies set up by the Department to assist research in specific branches of science or industry and promote the practical application of its results. The intention of the Department was not merely that the Board should review the metallurgical work in progress in Government laboratories, but that it should also arrange, as far as possible, for exchange of information with industry and for co-operation in metallurgical problems calling for investigation. For this purpose the Board is composed not only of departmental and university members, but also of prominent representatives of industry.

The metallurgical industries have already been provided with access from many sources to information upon research undertaken in Government institutions; the more pressing task before the Board has therefore been to find out how it could most effectively assist these industries as a whole in dealing with their own research problems. It was clearly not for the Board to concern itself with everyday problems which industry has to solve in the ordinary course, nor could much ground be covered merely by waiting for industrial problems to be referred to it for assistance. If the research requirements of the country, both from the Government and from the industrial point of view, were to be seriously considered, the first requirement was plainly that a really "national" programme of research should somehow be drawn up. At the same time it was clear that the industrial side of the programme could only be supplied by industry itself. If once a genuine conspectus of the most pressing needs of the industry could be achieved it would then, and only then, be possible by co-operation to ensure that plans were made to cover the whole field of research work.

The readiest means of arriving at industry's outstanding problems was to call in the assistance of the research associations more particularly concerned with the metal industries; it was therefore arranged with the Research Council of Iron and Steel Manufacturers, the British Non-Ferrous Metals Research Association, and the British Cast Iron Research Association that they should take steps to bring together the problems which appeared to be most generally important to the progress of their own industries, leaving out of account such problems as they would expect to attack as part of their own programme.

Lists of investigations were accordingly drawn up by each Association after the fullest discussion, and from these separate lists, each representing the considered requirements of a section of the industry, the final list was drawn up and submitted for the consideration of the Board.

Before accepting the list as the completest account at present possible of the general research requirements of the industry, the Board submitted it confidentially to a large number of representative metallurgists, both in the industry and the universities, for their criticisms. As a result it was still further revised and it has now been given the widest circulation practicable.

The list in its final form covers a wide field, including, as it does, such subjects, among others, as the thermodynamics and physical chemistry of metallurgical reactions, gases in metals, surface films, oxidation and scaling of heated solid metals, mechanism of age hardening, intercrystalline failure, welding, surface finish, and refractories, and it may now be taken to represent the best conspectus the Board is at present able to achieve of the problems which most need solving in the interest of industrial progress. A certain number of specific proposals for investigation have also been added to the list as examples of problems which might well be investigated by those who could not, in the nature of things, undertake the major inquiries. It is hoped that the circulation of the list will be effective in concentrating interest in the directions when further effect is required and in promoting arrangements for the undertaking of research wherever this is necessary.

Meanwhile the Board has already been endeavouring, in direct collaboration with interests specially concerned, to prepare the ground, by discussion and review of existing knowledge, for an attack upon several of the problems included in the programme; and it is proposed in a further article to give some account of the steps which are being taken in concert with industry.

The Action of Aluminium in Nitride Hardening.

ALTHOUGH nitride hardening is extensively practised, the precise nature of the hardening mechanism is not fully understood, and whilst it is known, for example, that the addition of small amounts of hardening elements, such as aluminium, to the steel improves the quality of the nitrided case, the manner in which this is effected has not been determined. There appears to exist some similarity between the mechanisms of nitride hardening and age hardening. In the latter, hardening may occur as the result of the precipitation from solid solution of a finely dispersed phase or the transformation of an already existing phase. Similarly in nitride hardening, according to Fry, aluminium nitride may be precipitated during nitriding, and give rise to the hardening effect. An alternative explanation is that aluminium atoms are substituted for some of the iron atoms in the iron-nitrogen phases, the marked increase in hardness, as compared with the aluminium-free alloys, being attributed to the severe distortion of the lattice arising out of the presence of the aluminium atoms.

Which of these two explanations is the correct one should be capable of experimental determination, and an X-ray study of the problem to this end has been made by J. T. Norton and is described in Technical Publication No. 550 of the American Institute of Mining and Metallurgical Engineers. The lattice structures of aluminium-free alloys of iron and nitrogen have already been investigated by Eisenhut and Kaup, and also by Hägg, and since the results have been confirmed by Norton, the diagram put forward by Hägg was accepted as a working basis. If the substitution theory were correct, the several phases which are present should occur also in the alloys containing aluminium, but with parameters enlarged by an amount proportional to the quantity of aluminium present. Increasing lattice distortion would be indicated by an increase in the broadness of the diffraction lines, although the homogeneous ranges may not be materially changed. If the precipitation theory were correct, the addition of nitrogen would result in the precipitation of aluminium as the compound Al N and the iron-nitrogen phases would only be formed after this compound had

been precipitated from solid solution. The lattice constant of the solid solution should revert to that of pure iron, and thereafter when the iron-nitrogen compounds were formed, the lattice parameters should be the same as in the straight iron-nitrogen alloys, and those phases would be homogeneous at nitrogen contents greater than in the iron-nitrogen alloys by an amount equal to that combined with the aluminium, provided that iron and aluminium form separate and independent phases with nitrogen.

Since X-ray studies of the surface layers of nitrided samples were considered to be unsatisfactory because of the broad diffraction lines which result, powdered samples were used in the investigation. Alloys of iron and aluminium were made by melting the pure metals in vacuo in a high-frequency furnace. They were then reduced to a powder which would pass a 200-mesh sieve and were nitrided in powder form. In the first series of experiments the precipitation of aluminium nitride was studied on alloys containing up to 10·1 per cent. aluminium, X-ray photograms being taken before and after nitriding at 800 deg. Cent. for twenty-four hours, since this treatment produces only a very small amount of nitrogen in the iron phase. The results showed that in each case all of the aluminium had been precipitated as Al N, and the next series of experiments were undertaken to show that the lattice parameters of the various iron-nitrogen phases were independent of the aluminium content of the alloys. Several series of iron-aluminium alloys were nitrided at different temperatures to obtain a wide range of nitrogen contents. The lattice constants of the homogeneous gamma phase, which has a face-centred cubic structure, were determined, and the results obtained demonstrated the independent nature of the iron and aluminium phases. In the hexagonal epsilon phase in the straight iron-nitrogen alloys, the lattice constants change appreciably over the homogeneous range, which extends from 8 to 10 per cent. nitrogen. At the lower nitrogen value the parameters were found to be independent of the aluminium content. Agreement was also established at the higher value, but the observed nitrogen contents were lower than the calculated values, which is due possibly to non-homogeneous nitriding of the individual grains of powder. At the low nitriding temperatures necessary to produce high nitrogen contents, this effect is to be expected, and agrees with the observation in practical nitriding that aluminium retards the diffusion of nitrogen. It was not found possible to obtain a high enough nitrogen content with more than 1 per cent. aluminium present for the zeta phase to appear, because of the effect of aluminium in retarding nitrogen diffusion. Aluminium nitride is crystalline and its structure is known, but the fact that no diffraction lines corresponding to this phase were obtained in the photograms is attributed to its occurrence in a state of subdivision too fine to be detected in this way, but the indirect evidence of its presence is conclusive.

The experimental results generally confirm the precipitation theory as the principal cause of nitride hardening, evidence being obtained (*a*) of the definite removal of aluminium from solid solution, (*b*) that the lattice parameters of the iron-nitrogen phases are quite independent of their aluminium contents, and (*c*) that the nitrogen contents of the various phases are in complete agreement. The evidence not in agreement is that, with the higher aluminium contents and lowest nitriding temperatures (about 400 deg. Cent.), the nitrogen content of the alloys is slightly too low, a fact which might be ascribed to the inhibiting action of aluminium nitride on the diffusion of nitrogen. The distortion of the lattice structure by the compound Al N may also be a factor in lowering the amount of nitrogen that the lattice is able to retain. The evidence both from the experimental work and from practical nitriding experience indicates that the precipitation in a finely divided form of Al N in the iron matrix during nitriding is the chief cause of hardening, and that the presence of nitrides of iron is a factor of relatively small importance in causing hardening.

The Corrosive Action of Brines.

AT the tenth World Dairy Congress, held in Rome and Milan between April30th and May 6th, Messrs. A. Burr and M. Miethke presented a paper on "The Corrosive Action of Brines upon the Metals Used in Dairies." The paper is reported in *Alluminio*,* the official organ of the National Fascist Association for the Italian Metallurgical Industry, from which the following notes are taken.

The behaviour of metals under the action of the following brine solutions has been studied :—

(I) Reinhartin 28° Bé Kühlsohle A.G., Leipzig ; this brine is principally composed of $CaCl_2 6H_2O$ and $MgCl_2 6H_2O$ in the proportion 1 : 3. It also contains protective colloids and expanding substances.

(II) Chrome Reinhartin 27° Bé of the same firm ; this solution has the same composition as the preceding, with the addition of sodium chromate.

(III) Termolite, 22° Bé, a solution based on calcium and chlorine, manufactured by the Kühlsole A.G., of Leipzig.

(IV) Brine for the dairy industry, 36° Bé, a product of the same firm ; contains carbonate with an addition of silicate.

(V) Refrigerating brines, 22° Bé.

(VI) Special refrigerating brine, 19° Bé, made by the Internationale Chemie A.G., Harburg-Wilhelmsburg ; composed of $CaCl_2 6H_2O$ and $MgCl_2 6H_2O$ in the proportion of 1 : 3. This solution produced white precipitates of silicates.

(VII) Frigisol, 22° Bé, made by Gebrüder Bayer, Augsburg. This solution is also composed of $CaCl_2 6H_2O$ and $MgCl_2 6H_2O$ in the proportion of 1 : 3·7, but it contains also sodium chromate, which affords a protection against corrosion.

(VIII) Eissol, 22° Bé, made by Alfred H. Goldenpfenning, Schönebeck a/Elbe. It is composed of $CaCl_2 6H_2O$.

(IX) Frigodur, 22° Bé, Müller and Schauerte, Düsseldorf, also composed of $CaCl_2 6H_2O$.

(X) A 22° Bé solution of $CaCl_2$.

(XI) A 22° Bé solution of $MgCl_2$.

(XII) A 22° Bé solution of kitchen salt and Salgemma.

METALS AND METHODS.

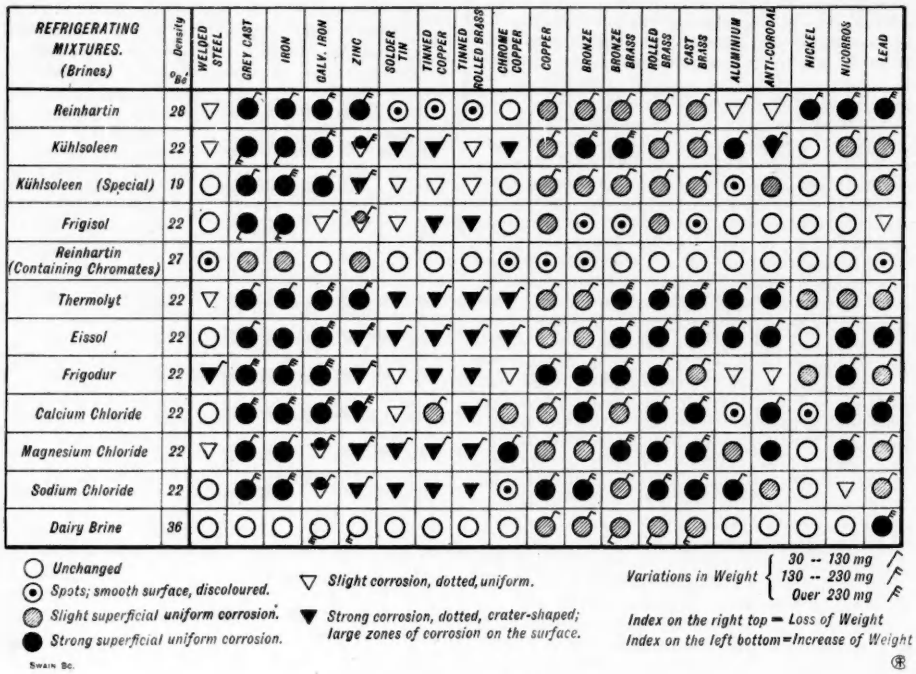
Experiments were carried out with V_2AE, iron, grey casting, galvanised iron, zinc, soldered tin, tinned copper, tinned brass, chrome copper, copper, bronze, aluminium brass, anticorodal, which is an alloy of Al, Ni, and a nickel *nicorros*—Pb alloy. All these metals were of the standard quality as obtainable in commerce. Sheets of these metals of about 100 square centimetres were kept half-immersed in

* *Alluminio*. Milan, March-April, 1934.

glass containers of 1 litre capacity into which ½ litre of solution was poured. The solution was kept in agitation and air saturation by continuous stirrers. The experiments lasted thirty days and during the whole time the temperature was kept at —5 deg. Cent. The usual precautions in such tests were observed.

The authors present the results in the form of a chart, which we reproduce.

They point out that the variations in weight by themselves cannot give an exact idea of the damage caused by corrosion, for the losses of weight may be partially balanced by the products of corrosion which adhere to the sheets and which it was impossible to remove with the brush. It is for this reason that the conditions of the plates are indicated in the diagram. These signs refer only to those parts of the sheets which were immersed in the solution.



MEANING OF THE SYMBOLS

The authors make the caveat that only the action of such brines as have the same Beaumé should be compared. This is indispensable, because not all brines have the same density of 22° Bé. The Reinhartin and chrome Reinhartin had 28 and 27 Bé, the "dairy" brine 36, and the special Kühlsoleen only 19° Bé. When these circumstances are taken into account the following conclusions are reached:—

The chrome Reinhartin and the "dairy" brine are the most favourable solutions. The highest losses in weight observed with chrome Reinhartin were only about 30 mg. on zinc.

The losses in the case of iron and lead were about 20 mg.; on the lead a stratum containing chrome and on the iron a stratum of rust was observed.

The aspect of nearly all other metals remained practically unaltered.

The "dairy" brine attacked copper and its alloys (brass and bronze) and, in a higher degree, lead. The other metals did not change their aspect.

The cause of the heavy losses in weight observed in metals not combined with others (particularly zinc), must be sought in the presence of a strong, adherent, and resistant crust which formed itself on the parts of the metals which were not immersed in the solution.

The chrome-containing Frigisol comes second. This solution contains smaller quantities of chromium than the chrome Reinhartin; the chromium therefore offers here less protection. It is surprising that the chromium should have violently affected the soldered tin and the galvanised sheets, a fact which the authors have established by the considerable losses in weight and by the large fields of corrosion. The corrosive effect was particularly noticeable on iron, grey casting, zinc, and lead.

The special Reinhartin ranks last. It behaves favourably with galvanised sheets and tin. It attacks Al and Pb more strongly, whilst Ni, *nicorros*, and the V_2A steel remain unaffected.

Less favourable was the action of Kühlsoleen of the same firm; nearly all the metals appeared to have been strongly attacked. This solution represents, therefore, a transition between the previously mentioned brines and those composed of $CaCl_2 6H_2O$, $MgCl_2 6H_2O$ and kitchen salt, which occupy the last place. Nearly all these brines behave practically in the same manner and attack metals in a greater or less degree.

The authors point out in conclusion that their results do not negate the possibility of using any of the brines if they are associated with the right metals.

Practical Cupola Control.

By C. C. DOWNIE.

Probably the most disconcerting feature in the scientific handling of the cupola is that there is no method of ascertaining the composition of the metal until after most of the day's work has been completed. The reason for this is that the ordinary systems of chemical analysis are too involved, and require too much time to complete to be of immediate service. Cupola operation as a rule is left in the hands of more or less unskilled labourers, although the mixtures charged may be carefully calculated out. Iron castings for general engineering purposes are seldom specified to within very narrow limits, and a fairly wide margin is the rule, rather than the exception; but when it is desired to make high-class castings of thin section, the whole system of operating the cupola requires to be altered. Each charge is then weighed off individually, and introduced into the furnace in a predetermined order. As damp coke occupies an appreciably greater space than dry coke, the fuel is measured rather than weighed. That is, after weighing the usual amount of coke, a fixed number of shovelfulls which are required to fill a box of known dimensions are taken as the standard, and a certain number of them is apportioned per charge of iron.

In order to ascertain the approximate composition of the iron as it was tapped from the cupola spout, the following practical method was adopted. It is based on a method originally employed by large scrap dealers, and by metal refiners who examined their metal without the assistance of laboratory tests.

It is known that the sparks emitted from a grinding wheel differ widely when a variety of alloy steels is being ground—see The Metallurgist, August 29th, 1930, and The Engineer, February 21st, 1930. The presence of nickel-chrome, tungsten, molybdenum, and other steels in a scrap heap are approximately ascertained in this way to the present day. In cupola melting sparks are emitted at the tapping spout as the metal enters the ladle, and variations in them give a reliable indication of the silicon content of the metal.

Any operative who is engaged daily at the cupola is aware of the variation of the sparks emitted, but can seldom offer a satisfactory explanation.

To ensure accuracy, the conditions of noting this physical peculiarity must be standardised, and, further, the average results recorded must be periodically checked by ordinary chemical analysis. A definite area around the ladle is examined to note approximately how the sparks travel.

Method of Examination.

The tapping of the iron is best watched from the cupola charging floor. From this point, the filling up of the ladle may be examined without inconvenience, using melter's blue glasses.

The first tappings are ignored, as the metal is generally cold. Examinations are made from the tapping of the third ladle onwards. A profusion of sparks arises when the tapped metal first reaches the ladle, but no inference can be gathered from this display, as the metal may be either cold or hot. It is the consistent emission of sparks as the metal flows from the tapping spout to the molten iron in the ladle that is of importance. Iron which is low in silicon throws off sparks in a variety of forms. Where a comparatively high silicon content is present, this phenomenon will more or less disappear. The sparks are noted as stars, globules, and strands, as the case may be, but the most important point is that a profusion of sparks denotes a low silicon iron.

Each tapping of the iron to the ladle is examined, and the average result taken at the conclusion of the operations. This is compared with the silicon content as obtained from chemical analysis, and will be found in practice to be strikingly accurate. Much assistance can be gained by working on the same class of iron for an appreciable period, as a considerable alteration in the phosphorus content may adversely affect the results.

A high silicon iron seldom throws off many sparks, irrespective of the phosphorus content. Silicon has sometimes been regarded as a constituent which can confer fluidity, but practical experience has proved that high silicon irons are generally sluggish. The sluggishness of low-silicon irons is apt to be misinterpreted as they are more sensitive to chilling actions, and should be compared when they are in properly heated condition.

In noting the sparks emitted a record should be kept of the different tappings, the temperature of the metal, and the state of the weather. Great efforts were made by the author to find if it would be possible to ascertain the phosphorus content in an inverse manner, since phosphorus affects the sparking qualities of the silicon, but what little physical peculiarities were noted were of too indefinite a character, and it was found necessary to rely entirely on tedious chemical analysis.

Other Constituents.

The percentage of manganese in the iron can also be ascertained with great accuracy before being checked by chemical analysis. The surface of the iron as it fills up the ladle is examined and is seen to be either bright and clear or dull and covered with a film of oxide. Metal high in manganese content is invariably bright and clear, save when, and only when, the iron tapped is allowed to become unduly cold. When little manganese is present the surface of the iron readily becomes dull, and shows few, if any, patches of bright metal. As the manganese content is increased the film of oxide diminishes.

This film adopts geometrical forms which break up as the tapping proceeds, but the amount of surface which remains bright and clear is approximately constant. High-manganese irons are practically entirely free from anything in the nature of a film on the surface, if the tapped metal is anywhere near the recognised tapping temperature. With less than 0·3 per cent. the approximate determinations of manganese are apt to be doubtful, as below this content the surface is entirely covered with the film of oxide.

With more than 0·3 per cent. manganese little rifts appear in the surface, but these disappear in the film. They become more pronounced at 0·4–0·5 per cent. manganese. Above 0·5 per cent. the squares of film are observed to separate out and float to the side of the ladle, as the tapping proceeds. At 0·7 per cent. manganese the greater part of the metal surface displayed is bright and clear, and when the percentage approaches 1 per cent. there is no film to be seen. So far as the other constituents are concerned, phosphorus, sulphur and carbon appear to exert no influence whatsoever.

Another characteristic which a high-manganese content introduces is that the iron remains fluid much longer than do those of low manganese content.

Efforts were made to utilise this point for ascertaining approximate composition, but the results could not compare with those obtained from the surface as described.

When any dirt appears on the surface of a high-manganese iron it usually flits from side to side of the ladle, whereas with a low-manganese iron it is absorbed by the film of oxide.

As a confirmation of the manganese content the colour of the skin of the cast metal when cold is taken into account. It shows bluish grey when low in manganese, and brownish when high in manganese.

As regards sulphur, a wide series of tests were carried out, but there does not appear to be anything of a physical nature which can assist in determining this constituent. Attention was then given to the nature of the slag, and an approximate method was evolved following the practice adopted in non-ferrous blast-furnaces when dealing with "matte."

What happens when a high-sulphur iron is being tapped is that a proportion of the sulphur is expelled. The reason for the expulsion is that manganese sulphide rises to the surface and becomes oxidised as a result of exposure to the atmosphere. To gain a really accurate figure it is thus almost essential to work with irons of practically the same manganese content throughout. The sulphur content can then be determined to within fractions of 0·1 per cent. In the same manner as lead acetate soaked paper is used in the chemical laboratory for estimating minute proportions of hydrogen sulphide, so also is paper, immersed in coloured vegetable compounds, used for determining small quantities of sulphur dioxide. The bleaching effect which the gas exerts is quantitative, and the reduction in colour is proportional to the sulphur content of the iron.

There is only a very small proportion of sulphur in most cast irons used for general engineering purposes, and hence it is desirable to ascertain this with accuracy, but the foregoing test cannot compare with those for silicon and manganese.

As a means of confirmation the same bleaching test was applied to the slag. As the slag flowed from its tap hole it was sprinkled with water, and the steam which was evolved allowed to play on the coloured paper and the bleaching effect noted. A series of papers with the colour bleached were used as the standard, and the results were taken from the average obtained from both metal and slag.

CONCLUSION.

The advantage of ascertaining the approximate composition of the iron as tapped from the cupola will be at once acknowledged by those who have been engaged in the production of accurately made castings. Although the mixtures which have been introduced to the cupola may have been fully analysed, there is always a certain amount of odd scrap introduced which can readily alter the composition, since every little lot cannot be subjected to individual analysis. Hence the moulders have to accept the composition for granted, and this cannot be confirmed or refuted until after practically all castings have been completed, since the chemical analyses occupy the best part of two hours. When the foregoing method is adopted the examination of the preliminary charges reveals the approximate composition, and the succeeding charges are altered accordingly. After some experience, and with the results from examinations checked by analysis, a surprising degree of accuracy can be secured. Working with only infrequent analysis, the point of accuracy is never so readily earned and much longer practical experience is necessary. It is worth remembering in this connection that most ordinary chemical analyses are done on a small sample taken from some odd pieces of pig iron or scrap. The sample is taken as representing the whole charge, but in practice the contrary is much more often the case.

With the foregoing physical tests the whole bulk of the iron as it is tapped from the cupola spout is under survey, and it is contended that in many cases any slight inaccuracies are offset by the advantage of reporting on the whole of the contents.

The Age-Hardening of Steels.*

By R. HARRISON, B.Sc.

THE phenomenon of age hardening in mild steel is well known, and its explanation by the theory of the formation and retention of a supersaturated solid solution in α iron by quenching from below the Ac_1 temperature, followed by the breakdown of this

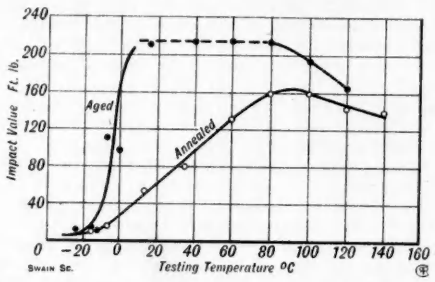


FIG. 1—*Steel No. 1 (C 0·03 per cent.). Charpy Impact Values at Various Temperatures. Standard B.S.I. test piece (10 mm. × 10 mm., with V notch ½ mm. root radius, 2 mm. deep).*

solution by ageing at atmospheric temperature, is now generally recognised.

At the Ac_1 temperature α iron can hold 0·035 per cent. carbon in solid solution, whereas the limit of solubility at 20 deg. Cent. is 0·008 per cent. carbon. The supersaturated solution obtained by quenching

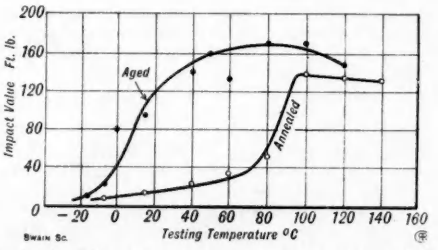


FIG. 2—*Steel No. 2 (C 0·045 per cent.). Charpy Impact Values at Various Temperatures. Standard B.S.I. test piece.*

in water from Ac_1 is unstable and breaks down at atmospheric temperatures, and the excess carbon is precipitated in a highly dispersed form, causing a marked increase in the Brinell hardness of the steel.

In the experimental results here put forward the

* Communication from the Research Department, Woolwich.

behaviour of steels, not only of low, but of medium carbon content is illustrated, particular reference being made to impact tests, to differences in the initial treatment before ageing, and to the effect of additions of manganese and chromium on the age hardening undergone.

EFFECT OF CARBON CONTENT.

Analyses of the steels used are given in Table I. All were annealed at 930 deg. Cent. and cooled in the furnace before being reheated to 680 deg. Cent. and quenched in water. This constituted the treatment preliminary to all ageing tests. Subsequent changes in the Brinell hardness and Izod impact figure are shown in Tables II and III.

TABLE 1.—*Chemical Analyses of the Steels.*

Steel No.	Carbon.	Silicon.	Manganese.	Sulphur.	Phosphorus.
1	0·03	<0·01	0·03	0·010	0·005
2	0·045	0·01	0·06	0·021	0·010
3	0·05	0·01	0·02	0·021	0·006
4	0·08	<0·01	0·32	0·033	0·015
5	0·09	<0·01	0·35	0·013	0·018
6	0·09	0·01	0·41	0·034	0·011
7	0·17	0·01	0·36	0·012	0·016
8	0·22	0·10	0·37	0·040	0·020

In the steels susceptible to age hardening the hardness increased and the impact value fell rapidly during the first fourteen days, after which little further change occurred before a stable condition was reached at the end of two months.

The amount of free ferrite, and hence the volume of solid solution formed, are reduced by carbon.

Increase in carbon content up to 0·09 per cent. resulted in an increase in the degree of age hardening and in the percentage increase in hardness. The amount of age hardening then remained about constant up to a carbon content of 0·22 per cent., but owing to the higher initial hardness the percentage increase fell.

EFFECT OF TEMPERATURE ON IMPACT FIGURE.

Notched bar impact tests were made in the Charpy machine at various temperatures, to determine at what temperature the rise in the impact value occurred in age-hardened steel. The results are given in Figs. 1 to 5. The impact figures corresponding to the steeply rising portion of the curves showed the usual "scatter," but the curves were drawn through the average of all values obtained at any one temperature.

When little age hardening had occurred (steels No. 1 and No. 2) the impact figure of the steel which had been aged after quenching from 680 deg. Cent. was at all temperatures much higher than that of the annealed steels. The effect of pronounced age hardening was to make the steel brittle ; or, in other words, to move the impact value-temperature curve to the right along the temperature axis, so that a high impact value was not obtained below 140 deg. Cent.

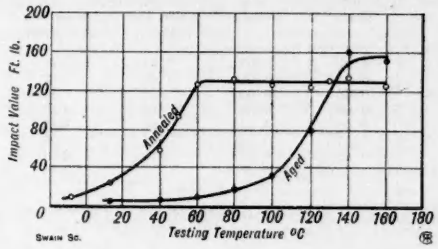


FIG. 3—*Steel No. 5 (C 0·09 per cent.). Charpy Impact Values at Various Temperatures. Standard B.S.I. test piece.*

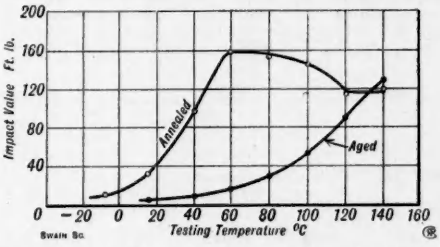


FIG. 4—*Steel No. 6 (C 0·09 per cent.). Charpy Impact Values at Various Temperatures. Standard B.S.I. test piece.*

EFFECT OF REHEATING BEFORE AGEING.

When the steels which had been quenched from 680 deg. Cent. were heated at 200 deg. to 400 deg. Cent. for one hour, and again quenched before ageing, they were found to be slightly softer or unchanged in hardness, and ageing was inhibited. It was not quite inhibited by heating at 100 deg. Cent., and began to appear after reheating to 500 deg. Cent., the effect increasing in magnitude as the reheating

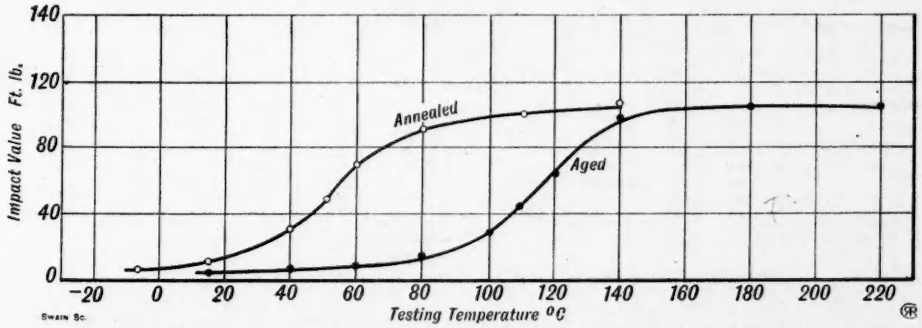


FIG. 5—*Steel No. 7 (C 0·17 per cent.). Charpy Impact Values at Various Temperatures. Standard B.S.I. test piece.*

TABLE II.—*Increase in Brinell Hardness Numbers During Ageing at Atmospheric Temperature.*

Steel No.	Carbon per cent.	Manganese per cent.	Brinell hardness number.								Increase in hardness.
			As annealed, 930 deg. Cent.	As quenched from 680 deg. Cent.	After ageing at atmospheric temperature, days.						
					1	3	7	14	21	28	56	
1	0·03	0·03	84	98	98	101	101	—	101	101	101	3
2	0·045	0·06	80	95	97	97	105	106	108	110	112	17
3	0·05	0·02	82	98	—	107	—	117	—	122	129	31
5	0·09	0·35	90	127	131	131	164	178	182	178	182	55
6	0·09	0·41	83	107	—	114	—	135	141	149	150	43
7	0·17	0·36	107	135	135	145	162	177	172	185	187	52
8	0·22	0·37	118	150	154	—	179	190	191	192	195	45

TABLE III.—*Change in Izod Impact Values During Ageing at Atmospheric Temperature.*

Steel No.	Carbon, per cent.	Manganese, per cent.	Izod impact figures, foot-pounds.								Fall in impact value.
			As annealed, 930 deg. Cent.	As quenched from 680 deg. Cent.	After ageing at atmospheric temperature, age.						
					1	3	7	14	21	28	56	
1	0·03	0·03	26	97	94	93	103	99	101	95	101	0
2	0·045	0·06	19	96	93	85	97	97	94	94	98	0
3	0·05	0·02	17	46	—	—	—	—	49	—	—	0
5	0·09	0·35	64	34	36	25	10	6	6	5	5	29
6	0·09	0·41	77	45	—	—	—	—	4	—	—	41
7	0·17	0·36	23	21	16	13	7	4	5	4	4	17
8	0·22	0·37	35	45	—	—	—	—	—	13	9	36

TABLE IV.—*Percentage Increase in Hardness on Ageing Steel which had been Reheated and Quenched after Preliminary Quenching from 680 deg. Cent.*

Steel No.	Carbon, per cent.	Manganese, per cent.	Reheating temperature, deg. Cent.							
			Not reheated.	100.	200.	300.	400.	500.	600.	700.
1	0·03	0·03	3	14	0	0	9	0	14	32
2	0·045	0·06	18	13	0	0	0	8	18	39
3	0·05	0·02	37	0	0	0	14	14	14	32
5	0·09	0·35	43	46	0	0	16	20	24	42
6	0·09	0·41	45	5	0	0	13	16	29	47
7	0·17	0·36	38	27	0	0	0	0	28	44

TABLE V.—*Izod Impact Figures After Reheating and Quenching the Material Previously Quenched from 680 deg. Cent.*

Steel No.	1		2		3		5		6		7	
Carbon, per cent.	0·03		0·045		0·05		0·09		0·09		0·17	
Manganese, per cent.	0·03		0·06		0·02		0·35		0·41		0·36	
Reheating temperature deg. Cent.	As quenched.	Aged.	As quenched.	Aged.	As quenched.	Aged.	As quenched.	Aged.	As quenched.	Aged.	As quenched.	Aged.
Not reheated	97	101	96	98	46	49	34	5	45	4	21	4
100	98	106	102	103	59	43	32	5	53	8	20	5
200	92	93	81	79	50	54	37	29	72	56	24	20
300	101	100	88	100	34	20	37	40	71	60	21	25
400	101	98	97	97	17	11	46	36	61	46	28	25
500	98	48	101	72	23	18	38	26	61	55	27	17
600	97	105	94	100	57	57	24	8	57	15	27	6
700	95	23	95	85	49	38	10	3	49	3	8	4

TABLE VI.—*Effect of Repeated Quenching, and of Time of Heating, on Ageing.*

Condition.	No. 1: C 0·03, Mn 0·03%.		No. 7: C 0·17, Mn 0·36%.	
	Brinell hardness.	Impact figure.	Brinell hardness.	Impact figure.
		Foot-pounds.		Foot-pounds.
Q. six times from 660 deg. Cent. (total time at 660 deg. Cent., 1 hour)	96	96	132	19
Q. six times from 660 deg. Cent. and aged	149	103	181	4
Q. 660 deg. Cent. (1 hr.) and aged	101	101	187	4
Q. 660 deg. Cent. (2 min.) and aged	110	110	183	4

TABLE VII.—*The Effect of Storage Temperature on the Age Hardening of Steel No. 5 (C 0·09 per cent.).*

Condition.	As quenched from 710 deg. Cent.	Quenched and aged one month at −80 deg. Cent.	Quenched and aged one month at −80 deg. Cent. followed by ageing one month at 0 deg. Cent.	Quenched and aged one month at 15 deg. Cent.
Brinell hardness	133	132	179	204
Izod impact figure	17	24	4	4

TABLE VIII.—*Steel No. 4. Effect of Cooling Rate from 900 deg. Cent. before Quenching from 680 deg. Cent.*

Heat treatment prior to quenching in water from 680 deg. Cent.	Brinell hardness.		Izod impact figures.	
	Tested immediately.	Tested after ageing two months.	Tested immediately.	Tested after ageing two months.
Water quenched from 900 deg. Cent.	132	140	108	97
Air cooled from 900 deg. Cent...	130	190	100	34
Slowly cooled in furnace from 900 deg. Cent.	124	192	94	6

TABLE IX.—*Age Hardening after Quenching and after Cold Working. Brinell Hardness Numbers.*

Steel No.	Carbon, per cent.	Manganese, per cent.	Treatment.	As quenched or rolled.	Aged two months.	Increase due to ageing.	Sum of separate effects of quenching and rolling.
8	0·22	0·37		151	181	30	—
9	0·23	1·42	Quenched in water from 660 deg. Cent.	161	173	12	—
10	0·23	2·10		201	204	3	—
8	0·22	0·37	Cold rolled	155	166	11	—
9	0·23	1·42	10 per cent. reduction in thickness ..	177	184	7	—
10	0·23	2·10		236	241	5	—
8	0·22	0·37	Quenched in water from 660 deg. Cent.	183	221	38	41
9	0·23	1·42	and then cold rolled 10 per cent.	202	226	24	19
10	0·23	2·10	reduction in thickness	226	237	11	8

TABLE X.—*Chemical Analyses.*

Steel No.	Carbon.	Silicon.	Manganese.	Sulphur.	Phosphorus.	Chromium.
8	0·22	0·10	0·37	0·040	0·020	—
9	0·23	0·18	1·42	0·040	0·030	—
10	0·23	0·22	2·10	0·030	0·020	—
11	0·32	0·12	0·49	0·037	0·022	—
12	0·29	0·04	0·42	0·045	0·020	0·87

TABLE XI.—*Brinell Hardness Numbers. Effect of Manganese.*

Steel No.	Carbon, per cent.	Manganese, per cent.	Brinell hardness.		Increase in Brinell hardness.
			As quenched from 680 deg. Cent.	Quenched and aged two months.	
8	0·22	0·37	147	200	53
9	0·23	1·42	168	197	29
10	0·23	2·10	191	198	5

TABLE XII.—*Izod Impact Figures. Effect of Manganese.*

Steel No.	Manganese content, per cent.	As quenched from 680 deg. Cent.	Quenched and aged two months.	Slowly cooled ½ deg. Cent. per minute from 680 deg. Cent.
8	0·37	38	7	41
9	1·42	69	22	28
10	2·10	67	61	16

TABLE XIII.—*Brinell Hardness Numbers. Effect of Chromium.*

Steel No.	Carbon content, per cent.	Chromium content, per cent.	As quenched from 680 deg. Cent.	Quenched and Aged 2 months.	Increase in Brinell Hardness.
11	0·32	—	170	187	17
12	0·29	0·87	170	177	7

temperature, followed by quenching, approached 700 deg. Cent. (Table IV). Corresponding impact tests are given in Table V.

Age hardening after quenching of steels Nos. 1 and 2 at 700 deg. Cent. was greater than after the initial quench at 680 deg. Cent.; that of the other steels was similar.

EFFECT OF REPEATED QUENCHING.

Whiteley[1] has shown that repeated quenching from 680 deg. Cent. has a marked effect on the disposition of cementite in mild steel, and it was thought that the results obtained with steels Nos. 1 and 2 might be due to this cause rather than to the higher quenching temperature used.

To determine the effect of repeated quenching, steel No. 1 together with steel No. 7 as a check were quenched in water from 660 deg. Cent. six times. The specimens were kept in the salt bath at 660 deg. Cent. for ten minutes before each quench, and after quenching they were dried and immediately returned to the salt bath. The results given in Table VI confirm the possibility of obtaining an increase in hardness in steel No. 1, the ageing of steel No. 7 being unaffected by this treatment.

The same effect could not be obtained merely by extending the time of heating at 660 deg. Cent. Age hardening was no greater after heating for sixty minutes at 660 deg. Cent. than after heating for two minutes, and was not much less after heating for only thirty seconds.

PREVENTION OF AGE HARDENING BY STORING AT LOW TEMPERATURES.

Low storage temperatures inhibit the changes which take place during ageing (Table VII). At −80 deg. Cent. age hardening was completely suppressed, whilst at 0 deg. Cent. the action proceeded, though possibly less rapidly than at atmospheric temperature.

EFFECT OF RATE OF COOLING IN THE PRELIMINARY HEAT TREATMENT AT 900 DEG. CENT.

Koster has published[2] some results showing that if a steel is quenched instead of cooled slowly from above Ac_3 no age hardening takes place after subsequent reheating and quenching from 680 deg. Cent. This effect of preliminary treatment was examined by attempting to age harden steel No. 4 (carbon, 0·08 per cent.) after it had been cooled at three different rates from 900 deg. Cent. The results given in Table VIII show that no age hardening takes place when the steel is originally quenched in water from 900 deg. Cent., and that the effects of ageing are slightly greater when the steel is slowly cooled in the furnace than when it is air cooled from 900 deg. Cent.

AGE HARDENING AFTER COLD WORKING.

The results given in Table IX (obtained on steels which had been annealed at 930 deg. Cent.) suggest that the age hardening which occurs after cold working is independent of that which occurs after quenching from 660 deg. Cent. The age hardening obtained in material cold worked after quenching was as great as the sum of the individual effects which were observed after quenching and after cold rolling separately.

In these results the inhibitive effect of manganese in age hardening was observable.

[1] *Journal*, Iron and Steel Institute, 1927, II, CXVI.

[2] *Archiv für das Eisenhüttenwesen*, 1928–29, No. 2, p. 503.

THE INFLUENCE OF MANGANESE AND CHROMIUM.

Manganese and chromium both reduce the carbon content of the eutectoid, and in this respect may be expected to have the same effect as an increase in carbon content. Further, Whitely[3] has shown that over 1·0 per cent. of manganese prevents the coalescence of the carbide, probably by lowering its solubility in ferrite. Hardness tests on steels containing manganese (Table X) show that increasing the manganese content from 0·37 per cent. to 1·42 per cent. greatly reduces the susceptibility to age hardening, and that when the manganese content is increased to 2·10 per cent., there is practically no increase in hardness after ageing (Table XI).

Izod impact tests are in accordance with changes in hardness, and from the last column in Table XII it may be noted that susceptibility to temper brittleness increases as the susceptibility to ageing decreases.

The influence of chromium has only been investigated in the case of one steel containing 0·87 per cent. of chromium. The effect of the age-hardening treatment on the Brinell hardness of this steel is compared in Table XIII with a steel having a slightly higher carbon content, but without chromium. The results show that practically no age hardening occurs in a steel containing 0·29 per cent. carbon and 0·87 per cent. chromium.

The inhibiting action of manganese and chromium is not completely explained by the lowering of the eutectoid composition. If allowance is made for the alloy contents, steels Nos. 10 and 12 may be regarded as equivalent to a steel containing 0·33 per cent. carbon and no manganese or chromium, when they should show an increase in hardness of the same order as steel No. 11. It would appear, therefore, that these elements also affect the course of the solid solubility curve of carbon in α iron, or the stability at atmospheric temperature, of the supersaturated solution.

Anodic Oxidation.

ONE of the chief difficulties associated with the electro-deposition of other metals on to aluminium is due to the presence of a thin oxide layer which is formed when the surface of the metal is exposed to the atmosphere. It is possible, however, to make use of such an oxide layer for the protection of aluminium and aluminium alloys against corrosion. The method now used consists of anodically oxidising the metal in a suitable electrolyte, and whilst it has been known for many years that oxide coatings could be formed on aluminium electrolytically, it is only comparatively recently that suitable industrial processes have been developed. The protection afforded the basis metal by the presence of such an oxide film or layer at the surface is very considerable, and has resulted in a wide application of the process to aluminium and aluminium alloys exposed to marine conditions. The film can be readily dyed, and this has resulted in the use of the metal so treated for ornamental purposes. The development and commercial exploitation of anodic oxidation can, in fact, be regarded as a contributory factor to the more extended use of aluminium and its alloys, and the subject has been surveyed generally in a paper

[3] *Journal*, Iron and Steel Institute, 1929, II, CXX.

presented by S. Wernick to the Electro-depositors' Technical Society in April last.

In the commercial development of the process, different electrolytes have been used in different countries, and amongst the best known and most satisfactory are chromates, sulphates, oxalates, and phosphates. The appearance of the film varies with the electrolyte, whilst its properties, such as thickness, compactness, hardness, adsorptive qualities, and electrical insulation characteristics depend largely on its method of production. In this country most of the commercial anodic oxidation has until recently been effected with chromic acid electrolytes, but sulphuric acid processes have now been introduced with varying degrees of success. In the process which was developed by Bengough and his collaborators, a 3 per cent. chromic acid solution, free from sulphuric acid and sulphates, is used, and the voltage is carefully raised in the first fifteen minutes to 40, at which it is maintained for thirty-five minutes, and then it is increased during the next five minutes to 50, and retained there for the last five minutes. The working temperature of the bath is about 45 deg. Cent., and carbon or stainless steel anodes are employed, the latter being more convenient for handling. The oxide coating produced on aluminium is grey in colour, and is darker with increasing quantities of alloying elements in the metal, this effect being especially marked in the case of silicon. While the chromic acid process produces satisfactorily protective coatings on aluminium, and many of its alloys, there are associated with it some practical limitations. The method of operation necessitates complete loading and unloading at not less than hourly intervals, and it is not possible to introduce into the bath material for treatment except at the initial stage. The process is further limited to the treatment of alloys of aluminium containing not more than 4 to 5 per cent. of heavy metals. Because of the porous nature of the metal and consequent retention of electrolyte, aluminium alloy castings are rather difficult to treat satisfactorily by any anodic oxidation process. The extent of the difficulties encountered depend largely on the quality of the castings. If the electrolyte is not eliminated from the casting, it subsequently reacts with the metal and gives rise to the defect known as " spotting out." With a colourless electrolyte, a white coloured deposit occurs at the affected portion and may not be very noticeable, but when the deposit is coloured, as it is when chromic acid is used as electrolyte, its presence is very obvious. It is one of the advantages of the sulphuric acid processes that comparatively low and constant voltages can be employed, owing, chiefly, to the high conductivity of the electrolyte and the adsorptive property of the film. Since the film formation progresses into the metal, it is of the utmost importance to use an electrolyte which allows of electro-chemical action at the aluminium-film interface, the position of which changes as the operation proceeds. For the formation of thick films this condition is essential, and sulphuric acid has been found to be a very suitable electrolyte. In order to obtain films of high quality, every precaution must be taken to ensure scrupulous cleanliness at all stages, and to maintain suitable conditions in the electrolyte. The racks for holding the work should be made of aluminium to avoid contamination of the electrolyte with other metals. The work is cleaned in the initial stages with suitable organic solvents. Complete removal of all grease is essential, and the last traces are removed by treatment in a mild alkaline solution containing a suitable inhibitor. Faulty or defective film can be readily removed by simple immersion in a moderately heated caustic solution, or by electrolysis in a similar but less reactive solution, and since the metal is much more readily soluble than the film, the commencement of accelerated action serves to indicate when the film has been removed.

The protective value of the films against corrosion has been amply demonstrated, and good results have been obtained in service tests of two or three years' duration under varying conditions. The compact hard kind of film is more resistant to corrosion than the ductile variety. Increased protection is obtained with increased film thickness up to an optimum thickness of about 0·002 cm., and the protective qualities are still further increased by filling in the pores with such substances as lanoline. The protective quality of the film is largely dependent also on the manner in which it has been produced, and the extent to which precautions have been taken to secure correct pre-treatment, freedom from pores, and expulsion of electrolyte. The hardness of the film is stated to lie between that of quartz and corundum, and to approximate to the value of 8 on Mohs' scale. The resistance to abrasion which it possesses has been demonstrated by practical tests.

The film possesses very remarkable adsorptive properties which have been utilised for decorative purposes. The simplest method of colouring the film is by direct immersion in an aqueous solution of the dye. Although dyestuffs of many classes readily colour the film, only a few yield results which can be regarded as satisfactory. The film is most adsorptive immediately it is withdrawn from the electrolyte, and the adsorptive power rapidly decreases. Since it is sensitive to practically all adsorbable substances, such as greases, it should not come into contact with anything before colouring other than the rinsing and dye solutions. The dyestuffs which are used vary in concentration from about 0·01 to 5 per cent., and the depth of colour obtained depends on the nature of the electrolyte used in the production of the film, the film thickness, the concentration of the dyestuff, the temperature of the dye solution, and the length of time of immersion in the dye solution.

It is necessary to fix or seal the dye either by further absorption of a resistant material, or by a change in structure of the film. In the former method suitable organic or inorganic compounds are incorporated in the film; while change in the structure can be brought about by the application of superheated steam. The marked heat-radiating powers which aluminium oxide possesses can be increased by colouring the anodically produced film black. The films also are electrically insulating, and this property may reach a very high value which can be further increased, by impregnating the film with suitable insulating materials such as waxes and synthetic resins, to withstand voltages of the order of 2000.

Another application of anodic oxidation is in the prevention of rapid deterioration in the reflective power of polished aluminium, for it seems that the reflective power may be actually increased by anodic treatment, and the particular type of treatment for yielding the highest degree of reflectivity or light diffusion is now being investigated.

Vacuum Melting of Steel.

REFERENCE has already been made in THE METALLURGIST* to the large-scale development of a new technique of vacuum melting, originally applied to the melting of the rare metals and other small-scale work, making it possible to produce materials which cannot be obtained by other means. The work of Gruber and of Dayton has shown that the possibilities afforded by vacuum melting in the preparation of carbon-free alloys may be of industrial importance.

Experimental work on the melting of steels in vacuo has been mainly concerned with measurements of the quantity and composition of the gases extracted from the metal under reduced pressure and the simultaneous changes of composition which the metal undergoes. In a recent paper by Eilender and others† these changes have been followed in the heating, melting, and freezing of steel in vacuo. The composition of the charge, before and after it had been held in the molten condition, was determined, and the volume and composition of the gases evolved were ascertained and related to the melting procedure.

The changes which occur during melting in vacuo are discussed in the light of the chemical equilibria involved. For example, for the small partial pressure of CO in the furnace atmosphere there corresponds a minimum possible carbon and oxygen content in the metal, governed by the equilibrium constant

$$\kappa = \frac{p_{CO}}{[FeO]\,[C]}$$

The total oxygen in commercial steels includes oxygen present not only as FeO, but as silicate, aluminate, &c., in the form of suspended particles; and in vacuum melted steels a more or less marked, though, of course, small, reduction of the amount of these particles is to be expected. The changes in hydrogen or nitrogen content are indicated by the help of Sievert's square root equation

$$\kappa = \frac{[X]}{\sqrt{p_{X_2}}}$$

where [X]=concentration of hydrogen or nitrogen in the metal and p_{X_2}=the partial pressure of these gases above the metal bath.

No hydrogen determinations were made in the course of the work described, but the carbon, oxygen, and nitrogen content of the resolidified carbon steels were found by the authors to show good agreement with the calculated limiting values. For alloy steels such calculations are not applicable on account of the formation of compounds between oxygen, nitrogen and carbon and the alloying elements; but in spite of this, a marked diminution in the total content of the compounds which form gases and of dissolved gases was to be expected, and was actually found in the vacuum-melted alloy steels.

The melting was carried out in a molybdenum-wound resistance furnace of about 7 kilos. capacity, supplied by the Rohn Vacuum-melting A.G., Hanau. The steel was melted in an alumina crucible, and temperatures were taken with a disappearing filament pyrometer through a quartz inspection tube. After the charge had been melted, the bath was in general held liquid for one hour to complete degassification, but a melting period of up to three hours did not result in any further increase in the degree of purity of the metal.

The oxygen content of the steel was determined by the vacuum-melting method of Meyer and Castro, and the nitrogen content estimated colorimetrically by the solution and distillation method of Wüst and Duhr. To some extent the oxygen and nitrogen contents given depend on the limits of accuracy of these methods of analysis, and they should therefore only be regarded as expressing the order of magnitude of the occurrence of these constituents. Nevertheless, it is clear from the results given in Tables I and II that by vacuum melting a considerable diminution of the oxygen and nitrogen content is brought about.

The results are discussed at some length by the authors. Hydrogen is held to have no direct de-

TABLE I.—*Carbon Steels.*

Melt No.	Charge.	Melted in.	Held molten.		Composition, per cent. C.	Si.	Mn.	O.	N.
3	Carbon steel	Vacuum	1½ hr.	Charge	1·01	0·12	0·35	0·0018	0·0033
				Melt	0·84	0·12	0·35	0·0005	0·0013
4	Steel F A H. I	Vacuum	1 hr.	Charge	0·05	0·01	0·45	0·0120	0·0018
				Melt	0·005	0·03	0·12	0·0012	0·0006
5	Steel F A H. I	Vacuum	3 hr.	Charge	0·05	0·01	0·45	0·0120	0·0018
				Melt	0·005	0·03	0·17	0·0090	0·0008
6	Steel F A H. I	Hydrogen	1½ hr.	Charge	0·05	0·01	0·45	0·0120	0·0018
				Melt	0·002	0·11	0·11	—	0·0015
7	Armco iron+7% Swedish pig iron	Vacuum	1 hr.	Charge	0·28	—	—	0·020	0·0028
				Melt	0·08	0·08	0·10	0·0009	0·0006
8	Steel F A H. II	Vacuum	1 hr.	Charge	0·03	0·01	0·47	0·021	0·0165
				Melt	0·009	0·03	0·32	0·0098	0·0031
9	Basic steel	Hydrogen	1 hr.	Charge	0·03	0·01	0·47	0·021	0·0165
				Melt	0·004	0·11	0·37	0·005	0·0025
								F A H	
10	Steel F A H. II+10% Swedish pig iron	Vacuum	1 hr.	Charge	0·35	—	—	0·021	0·0155
				Melt	0·22	0·09	0·22	0·0007	0·0014
								Basic steel	
21	Basic steel III+6% haematite+2% hammer-scale	Vacuum	1¼ hr.	Charge	0·30	—	—	0·025	0·0098
				Melt	0·10	0·09	0·55	0·0007	0·0008

* THE METALLURGIST, August, 1933, page 62.

† W. Eilender, A. von Bohlen u. Halbach, and O. Meyer, "Archiv für das Eisenhüttenwesen," 1933–34, 7, 493–497.

carburising action on the liquid steel, since methane cannot be formed at the temperatures involved. The effect of a hydrogen atmosphere in still further reducing carbon and nitrogen content is attributed to its diluting effect in lowering the partial pressure of carbon monoxide and nitrogen. Copious evolution of carbon monoxide for a similar reason assists in the removal of nitrogen. Basic steel which was remelted with additions of pig iron and hammerscale in vacuo, exhibited a very high nitrogen loss, resulting in a very low final nitrogen content (melt 21).

Similar features were observed with alloy steels (Table II), but it was not possible to attain to the same decrease in carbon, oxygen, and nitrogen content. Moreover, melting in hydrogen had no advantage over a plain vacuum melt. The stable compounds in the chromium steel bath—such as the carbide, nitride, and oxide—reacted on one another much more slowly than the iron oxide and carbon in the liquid carbon steels. Oxide additions did not reduce the carbon content so much as in plain carbon steels, the CO pressures corresponding to the reaction of chromium oxide and carbon were quite considerably lower than the pressure produced by the reaction between FeO and carbon; and the nitrogen pressure of the nitrogen-containing chromium steels was considerably lower than the nitrogen pressure which stands in equilibrium with molten nitrogen-bearing pure iron. The ready absorption of nitrogen by chromium steels is shown by melt 16.

The changes in gas content of the metal were also studied by measurement and analysis of the gases evolved. Gas evolution from a vacuum-melted basic steel (melt 20) is shown in Fig. 1. Unfortunately, the furnace itself gave off a considerable amount of gas, and it was therefore necessary to carry out blank experiments which involved heating the furnace with no charge of metal. The result of such a blank experiment applicable to melt 20 are shown in Fig. 2. In the empty furnace there was little gas of any kind given off below 1100 deg. Cent., the temperature reached after six or seven hours' heating; the small amount which was pumped off was mostly air. Hydrogen increased to a maximum at about 1100 deg. Cent. and then fell again. Carbon monoxide, derived from a reaction in the graphite-alumina mixture used to protect the heating tube, formed the bulk of the gas evolved at 1300 deg. to 1600 deg. Cent.

Turning now to Fig. 1, it is seen that so long as the total gas was very small, it consisted mainly of air, though water vapour accounted for a rise in hydrogen to a maximum at about 1100 deg. Cent. The percentage of carbon monoxide increased with rise in temperature, and just after fusion of the steel reached its highest value, viz., about 75 per cent. of the 3 litres per hour which was being pumped off. The total quantity of gas rapidly diminished within one hour of melting, the principal constituent still being carbon monoxide. Nitrogen content showed an increase near the melting point at a time when the

TABLE II.—*Alloy steels.*

Melt No.	Charge.	Melted in.	Held molten.		Composition, per cent. C.	Si.	Mn.	O.	N.
11	V 2 A, Cr 17·5, Ni 9·0%	Vacuum	1 hr.	Charge	0·26	1·52	0·63	0·013	0·088
				Melt	0·23	0·98	0·58	—	0·042
12	V 2 A (as above)	Hydrogen	1 hr.	Charge	0·26	1·52	0·63	0·013	0·088
				Melt	0·23	—	—	0·0125	0–032
13	V 2 A (as above)+2·5% FeO	Vacuum	1¼ hr.	Charge	0·26	1·52	0·63	0·013	0·088
				Melt	0·14	—	—	—	0·027
14	V 13 F, Cr. 12·8, Ni 0·18%	Vacuum	1¼ hr.	Charge	0·08	0·86	0·44	0·0046	0·0168
				Melt	0·02	—	—	0·0045	0·0046
16	V 13 F (as above)	Nitrogen at 200 mm.	¾ hr.	Charge	0·08	0·86	0·44	0·0046	0·0168
				Melt	0·05	—	—	—	0·041
17	K 25 O, Cu 0·2, Mo 0·37%	Vacuum	1 hr.	Charge	0·14	0·20	0·53	0·015	0·0042
				Melt	0·07	—	—	0·00016	0·0012
18	E F O 35, Cr 0·9, Ni 2·56%	Vacuum	1 hr.	Charge	0·12	0·21	0·52	0·0025	0·0051
				Melt	0·05	—	—	0·00027	0·0016
19	V 2 A, Cr 17·6, Ni 9·15%+1½% chromium oxide	Vacuum	¾ hr.	Charge	0·26	1·52	0·63	0·013	0·074
				Melt	0·18	1·16	0·46	0·0037	0·034
22	V 2 A (as above)+1% chromium oxide	Vacuum	1¼ hr.	Charge	0·26	1·52	0·63	0·013	0·074
				Melt	0·12	—	—	0·0026	0·018

REMARKS.—11, Melt boiled, further gas evolution during freezing; 12, melt quiet after ½ hr.; 13, melt very lively; 14, melt perfectly quiet; 19, not malleable; 22, malleable.

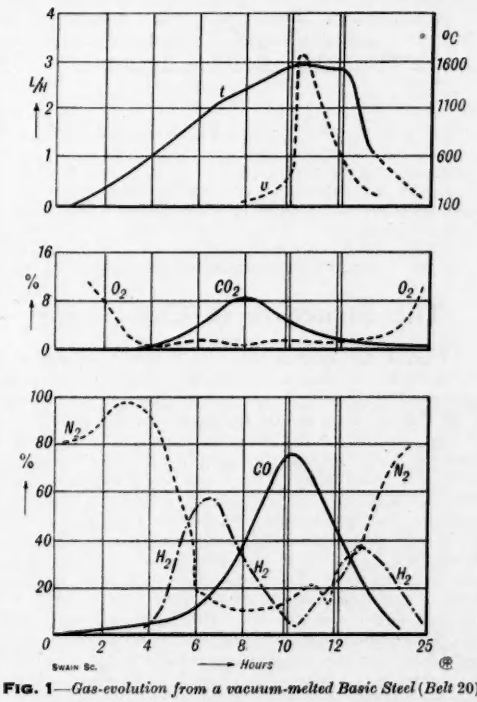


FIG. 1.—*Gas-evolution from a vacuum-melted Basic Steel (Belt 20)*

rate of evolution of gas was very high, so that a relatively large amount of nitrogen was being drawn off during the melting period. Thus, although the experimental data are to an unduly great extent influenced by the copious evolution of gas from the furnace

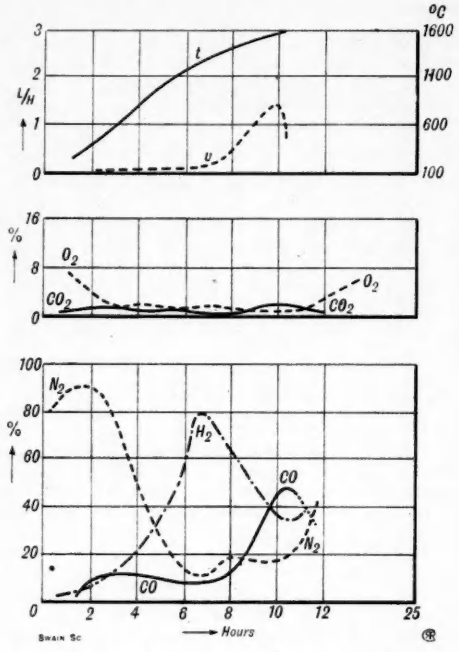


FIG. 2—*Gas-evolution in a blank experiment.*

materials, the data presented in Figs. 1 and 2, when combined, furnish some idea of the sequence and quantities of the individual gases evolved from the molten metal.

The Structure of Cast Iron.

AT the June Convention of the Institute of British Foundrymen at Manchester an interesting paper was presented by Dr. H. Nipper, of the Aachen Technical High School, on graphite formation in and structure of cast iron, including the results of recent work at Aachen on the influence of graphite size on the properties of cast metal. The principles of supercooling have been applied by various investigators to alloy systems, but the recognition in this country of the fine, sooty graphite obtained under certain conditions of melting in cast iron as a supercooled structure is due to Norbury.* The production of this particular form of graphite, designated "supercooled graphite," was, of course, not novel. It can occasionally be seen in old photo-micrographs, but its appearance had not given rise to comment. It had been obtained by Schuz in Germany by chilling a medium silicon iron, and Hanemann and Piwowarsky had studied the effect of superheating on graphite. Norbury showed that irons of the same composition made from mixtures of Swedish white iron and ferro-alloys could be made to yield entirely different graphite structures, according to the nature of the ferro-silicon used and to conditions of melting; that is, in effect, according to whether the conditions promoted or discouraged supercooling. In a supercooled structure the graphite is in an extremely fine, so-called eutectic, state of division, and in a structure in which supercooling does not arise the graphite tends to be coarse. The practical implication of this is of great importance, for it is now known that the composition of cast iron governs the mechanical properties mainly through its influence on the structure, and that other factors influencing structure have to be considered. The extent of supercooling depends upon the melting temperature and its duration; on the presence of constituents, solid, liquid, or gaseous, likely to nucleate the melt; on the rate of cooling, and on such influences as agitation of the metal. The effect of superheating is to promote the tendency to supercool. Dr. Nipper in his paper shows a photo-micrograph of flake graphite arising in a melt by nucleation from the furnace wall, and gives other photographs obtained from irons melted in a vacuum furnace (below 0·0001 mm. pressure), where the conditions, high superheat, and absence of gases, favoured a high degree of supercooling. The graphite structures resulting from the supercooling of hyper-eutectic, eutectic, and hypo-eutectic irons are described, and some interesting photographs are given of graphite taken by polarised light.

Investigations carried out on the effect of size of graphite on strength, wear, and corrosion show that a supercooled graphite is by no means the most useful form, partly because, as has been shown by Norbury, this fine graphite tends to be associated with ferrite. In practice it is extremely difficult to secure structures wholly supercooled, and mixed structures, in which a matrix of pearlite with flake graphite contains colonies of supercooled graphite with ferrite, are mechanically not satisfactory. It was to overcome the drawbacks of the ordinary supercooled structure that the idea of inoculation was developed, that is, artificial nucleation with a suitable graphitiser of a melt which, by virtue of its composition or method of melting or both, is likely to be supercooled. In this connection it should be noted that virtually every step taken to improve and refine cast iron tends to produce a supercooled structure. This particularly applies to furnaces offering high superheat to metal away from direct contact with fuel. Irons produced by inoculation processes are now commercially available, and show excellent mechanical properties, the graphite being intermediate in size between that of an ordinary engineering iron and the supercooled type, being otherwise uniformly pearlitic. In a paper recently delivered to the Iron and Steel Institute,† for such an iron made commercially by inoculating a suitable melt with nickel, Pearce records a tensile strength of 28·7 tons per square inch, with a Brinell hardness of 277 and a transverse rupture stress of 50 tons per square inch. This iron had, on a standard 1·2in. B.S.I. bar at 18in. centres, a total deflection of over ½in.

Reverting to the influence of supercooled graphite, Dr. Nipper quotes a recent investigation by Heimes and Piwowarsky on the effect of graphite size on abrasive wear, the composition being maintained the same. With graphite of increasing fineness, wear increased in various types of dry wear test. The lowest wear results were shown by well-formed and

* *Journal*, Iron and Steel Institute, Vol. 119, No. 1, 1929.

† *Journal*, Iron and Steel Institute, 1934.

relatively coarse temper carbon, and in grey irons the pearlitic structure gave the best results. Wallichs and Gregor in wear tests on various classes of cast iron for motor car cylinders also found that wear increases as the graphite becomes more finely disseminated and more linear. The best results were obtained with an iron with low carbon and lamellar pearlite, having a "moderate linear graphite dissemination."

Nipper and Piwowarsky have examined the effect of graphite fineness on corrosion, and arrived at the conclusion that corrosion is higher with very fine graphite and with a "high linear graphite dissemination," than with either temper carbon or short thick graphite flakes.

There is therefore evidence to show that extremely fine graphite of the supercooled type is not in many cases the most favourable, either chemically or mechanically, and that influences which promote supercooling, such as unrestricted superheating, are not in such cases advantageous unless steps are taken to offset the tendency to produce supercooled graphite. Bardenheuer and Zeyen have confirmed in Germany that excessive superheating is not advantageous in low carbon iron. Foundry control also requires to be modified if there is a risk of supercooling. Norbury has pointed out that supercooled irons are much more liable to chill than normal irons, and during the last few years it has been found in practice on a number of occasions that unexpected chilling, with, for example, highly superheated irons, is experienced with the production of such undesired results as inverse chill.

Much remains to be done before the complete theory of the cast irons is worked out, and doubtless contributions will be made both by British and German workers, for in both countries investigators are giving special attention to the problem. Its solution will almost certainly have reactions on a great deal of work that has been and is being done on *ad hoc* lines, in explaining apparent inconsistencies and indicating the line of future progress.

Pendulum Hardness Measuring Machines.

THE pendulum has been developed as an instrument for measuring hardness, in this country by Mr. Herbert and in France by Monsieur le Rolland, and an article in *Le Genie Civil** discusses the application of the machine designed by the latter to the measurement of superficial hardness and of the modulus of elasticity of materials.

At the outset it must be stated that the author seems to be hardly fair to Mr. Herbert, for he implies in the text that the use of a pendulum for measuring hardness and the elastic modulus is a new idea, and then, in a footnote, mentions Herbert's pendulum, but dismisses it with the statement that it differs in principle from that of le Rolland.

The method employed by Monsieur le Rolland for measuring superficial hardness consists in supporting a pendulum, through the intermediary of a diamond cylinder or ball, on the object whose hardness is required, and measuring the period of oscillation. The softer the body on which the pendulum swings, the faster it moves, *i.e.*, the smaller is its period of swing. This is due to the fact that contact is not made along a line (in the case of a cylinder) or at a point (in the case of a ball), but, owing to deformation of the sample, on a surface. Hardness is defined by the number of oscillations between two coincidences between the measuring pendulum and a standard one. It is claimed that it is purely the surface hardness that is measured, and, in the case where a ball support is used, that a surface of 1 square millimetre is sufficient for carrying out the test.

In connection with the use of the pendulum for measuring the elastic modulus, the author points out that Hooke's Law is not strictly true for certain metals, in particular for cast iron, the load/extension curve being concave towards the extension axis. The form of the curve can in general be determined on a tensile testing machine, but in the case of cast iron, this is practically impossible, owing to the low ductility of the metal. To employ the le Rolland pendulum a long bar of the material under test is rigidly fixed at one end, while to the other end is attached a cross bar on which are mounted two identically similar pendulums. One of these is set swinging, and it gradually transmits its energy through the support, causing the other one to swing, itself coming to rest when the second pendulum has reached a maximum. The process then reverses itself, the second pendulum transferring the energy back to the first one. It can be shown that the time t between two cessations of swing of one of the pendulums is given by the equation $t = E \div A$, where E is the modulus of elasticity and A is a constant. The following table shows for different metals the values found for the modulus by means of an extensometer and by the pendulum method :—

Metal.	Extensometer.	Pendulum.
Steel	20,830	21,000
Duralumin	7,760	7,640
Aluminium	7,660	7,650
Bronze A	11,990	12,000
Bronze B	12,900	12,500
Bronze C	9,800	9,600

The values obtained by the two methods are in reasonable agreement, and the author suggests that where they differ the pendulum results are to be preferred, as in this test the metal is much less deformed than in the extensometer test.

* *Le Genie Civil*, 1934, 104, 224.

Deoxidation of Red Brass.

THE presence of cuprous oxide in cast copper and its alloys may cause segregation and porosity, and so affect the mechanical properties. Deoxidisers are used to improve casting properties. For the deoxidation of red brass Reitmeister recommends the use of carbon monoxide in the nascent state produced by the addition of metallic oxide and carbon in molecular proportion. Nipper and Röntgen (*Die Giesserei*, March 2nd, 1934) have investigated the course of the reaction

$$Cu_2O + CO = 2\,Cu + CO_2.$$

In addition to the temperature, the reaction depends on the surface exposed, the degree of diffusion in the solid phase, and the concentration of the oxide. In carrying out the experiments the weight of the solid phase and its surface as well as the quantity and rate of the gas supply was kept constant. The gas pressure was easily regulated, as a molecule of carbon monoxide oxidises to a molecule of carbon dioxide.

Magnesia boats or crucibles and pure materials were used.

For the reduction experiments carbon monoxide was produced by the action of sulphuric acid on formic acid, and purified by means of caustic potash and pyrogallol. The gas was dried by calcium chloride and phosphorus pentoxide, and the evolution flask was evacuated before starting the reaction. After passing through the reaction tube the gas was collected in the analysis apparatus. The temperature of the reaction tube was regulated to ± 5 deg. at the low and ± 10 deg. at the high temperatures.

Reduction experiments were made at increasing temperature. A sample of 3·5 grammes of pure cuprous oxide in a magnesia boat was placed in the cold reaction tube and the whole system was evacuated and washed out with carbon monoxide. A stream of carbon monoxide was maintained at the rate of 50 ccs. in 3 min. The temperature was allowed to rise at the rate of 10 deg. per min. The experiment was discontinued when the gas contained less than 0·5 per cent. of carbon dioxide. A blank determination was made in order to allow for the vapour pressure of the saturated salt solution in the gasometer and the 50 per cent. caustic potash wash liquor.

Reduction experiments at constant temperature were carried out in a similar manner.

The same apparatus was used for oxidation experiments below the melting point of copper. Carbon dioxide was used as the reaction gas and copper ammonium chloride as the washing liquid. The charge consisted of 50 or 25 grammes of turnings of electrolytic copper which had previously been heated at 800 deg. to 900 deg. in a stream of hydrogen for two hours.

A vertical tube fitted with a water-cooled cap was used for experiments above the melting point of copper. A stream of carbon dioxide was circulated outside the reaction tube in order to minimise the danger of the diffusion of oxygen into the tube. Carbon dioxide was conducted into the molten copper by means of a magnesia tube for a period of one hour. A stream of the gas was maintained during the cooling of the sample.

Oxygen was estimated in the copper by a hydrogen reduction method. The sample was contained in a magnesia boat and was heated at a temperature of 800 deg. to 850 deg. for two hours.

In the reduction experiments, the formation of carbon dioxide began between 150 deg. and 200 deg., and reached its highest value at 600 deg. to 700 deg., with about 97 per cent. of carbon dioxide in the exit gas. The maximum reaction velocity was reached at about 500 deg. At 400 deg. the maximum amount of carbon dioxide in the exit gas was 4 per cent. At lower temperatures the reaction was very weak.

The oxygen value of the solid phase decreased rapidly with increase of temperature until it reached a small value, but the oxygen was never completely removed. At 1100 deg., after a heating period of one hour, the oxygen value had decreased to 0·30 per cent. corresponding to 2·82 per cent. cuprous oxide. At lower temperatures the reaction was more prolonged, and at 425 deg. the reaction was still perceptible after seven hours' heating.

Under practical conditions, however, the reaction proceeds more rapidly as the melt is violently agitated by the evolution of carbon dioxide. The deoxidation of oxide-rich copper melts by carbon monoxide is, therefore, a feasible proposition.

Further investigation, however, is necessary to determine how far the oxides of copper, tin, zinc, and lead can exist simultaneously in red brass, and the conditions under which their reduction may be accomplished.

The solubility of carbon monoxide and dioxide in molten copper alloys, according to published work, is doubtful. The latest work of Röntgen and Müller at Aachen indicates that for nitrogen, carbon monoxide, and dioxide no solubility exists even in impure copper containing sulphur and oxides. An increase of gas porosity owing to this cause is, therefore, not possible.

In oxidation experiments at temperatures below 700 deg. no oxygen absorption was detected. Above 800 deg. experimental difficulties were encountered with the apparatus, and the oxygen value of the copper was considerable, but no carbon monoxide was observed in the gas phase. These results were, therefore, not considered.

The authors obtained the equilibrium :

$$Cu_2O + CO = 2\,Cu + CO_2 \quad . \quad . \quad . \quad . \quad (1)$$

by combination of

$$Cu_2O = 2\,Cu + \tfrac{1}{2}\,O_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$2\,CO_2 = 2\,CO + O_2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The equilibrium constant from equation (1) is :

$$K = \frac{p_{CO}}{p_{CO_2}} = \frac{[CO]}{[CO_2]}$$

since copper and cuprous oxide are solid bodies and no volume change occurs. The equilibrium in equation (1) is obtained when the partial pressure of the oxygen from the dissociation of carbon dioxide balances that of the cuprous oxide.

The partial pressure of oxygen from equation (2) is p_{O_2}. In equation (3) it is :

$$p_{O_2} = K\,p_{CO_2}\left(\frac{p_{CO_2}}{p_{CO}}\right)^2$$

and from equations (2) and (3) combined :

$$K = \frac{[CO]}{[CO_2]} = \frac{p_{CO}}{p_{CO_2}} = \sqrt{\frac{K\,p_{CO_2}}{p_{O_2}}}$$

accordingly, $\log K = \frac{1}{2}(\log K\,p_{CO_2} - \log p_{O_2})$.

From the dissociation pressure of carbon dioxide, and the oxygen pressure of cuprous oxide, the equilibrium for equation (1) can be calculated.

For equilibrium at 1200 deg. the maximum proportion of carbon monoxide in the gas would amount to about 0·06 per cent. The results indicate that the affinity of carbon monoxide for oxygen is considerably greater than that of copper for oxygen.

The results of this work confirm those of Iwasé—Sc. Rep. Toh. Imp. Univers. 15 (1928), p. 531—who found that no dissociation of carbon monoxide occurred over red-hot copper, and also that the copper was not oxidised by carbon dioxide.

In equilibrium experiments of this type much may depend on reactions which occur between the refractories employed and the solid phase. The authors mention that the oxidation experiments at the higher temperatures were not successful. This may be due to reaction between the magnesia and the molten copper. The procedure adopted of passing the gas over the solid at a standard rate is probably the most satisfactory way of conducting such experiments. The fact that copper is not oxidised by carbon dioxide is of interest, but under industrial conditions oxygen is usually present in addition to carbon dioxide.